Efficient Singlet Fission at the Border of Order and Disorder

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Summary

Detailed understanding of defects and ordering within technologically relevant materials is key for future commercial implementation. Here, we highlight recent work by Volek *et al*. where singlet fission within rubrene crystals is explored through a combination of transient absorption microscopy and molecular dynamics simulations. Their results show that increased disorder at the crystals edge significantly enhances singlet fission.

Main Text

Defects or imperfections are often at the center of chemistry.[1] For example, atomic inclusions in form of color centers result in coloration of gemstones while surface defects can increase catalytic performance in heterogeneous catalysis. In photophysics on the other hand, defects are generally undesired as they can provide additional non-radiative relaxation pathways, reducing the yield of the desired processes.[2,3] Hence, great emphasis is placed on engineering materials to be free of defects to maximize performance. However, defects can also induce interesting optoelectronic properties and impact intermolecular coupling between adjacent molecules, leading to new, desirable properties.

Intermolecular coupling is the foundation of aggregation-induced effects including H- and J-type coupling,[4] excimer formation,[5] and critically impacts the rate and efficiency of triplet-triplet annihilation (TTA) and singlet fission (SF).[6] In SF, electronic coupling between two molecules facilitates the generation of two lower energy spin-triplet states from one high energy spin-singlet state in a spin-allowed electron transfer process.[1,7] To ensure energy conservation, an additional requirement is that the energy of the singlet state must be higher or equal to the combined energy of both triplet states: $E(S_1) \geq 2 \cdot E(T_1)$. TTA, on the other hand describes the reverse process, where two triplet states generate a singlet state.[6,8] To first approximation, it is expected that strongly ordered, crystalline structures have the highest efficiency of SF. However, as demonstrated recently by Roberts and co-workers,[1] this expectation is oversimplified, and SF rates can be enhanced in distorted regions due to symmetry breaking.

SF can occur either through a direct pathway, where a spin-correlated triplet pair state ^{1}(TT) is generated in a single step, or through an indirect pathway through a series of charge transfer (CT) states. The precise electronic coupling strength dictates the relative branching ratio of the two pathways. The electronic coupling is impacted by the molecular ordering within a crystal where strong spatial overlap of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of adjacent molecules is desired. Due to different symmetries of the HOMO and LUMO orbitals, slip stacking generally facilitates the required overlap. However, rubrene, the workhorse of TTA and a well-studied SF material, undergoes efficient SF despite a negligible spatial overlap of HOMO and LUMO enabled by *e.g.*, symmetry-breaking via vibrational modes.

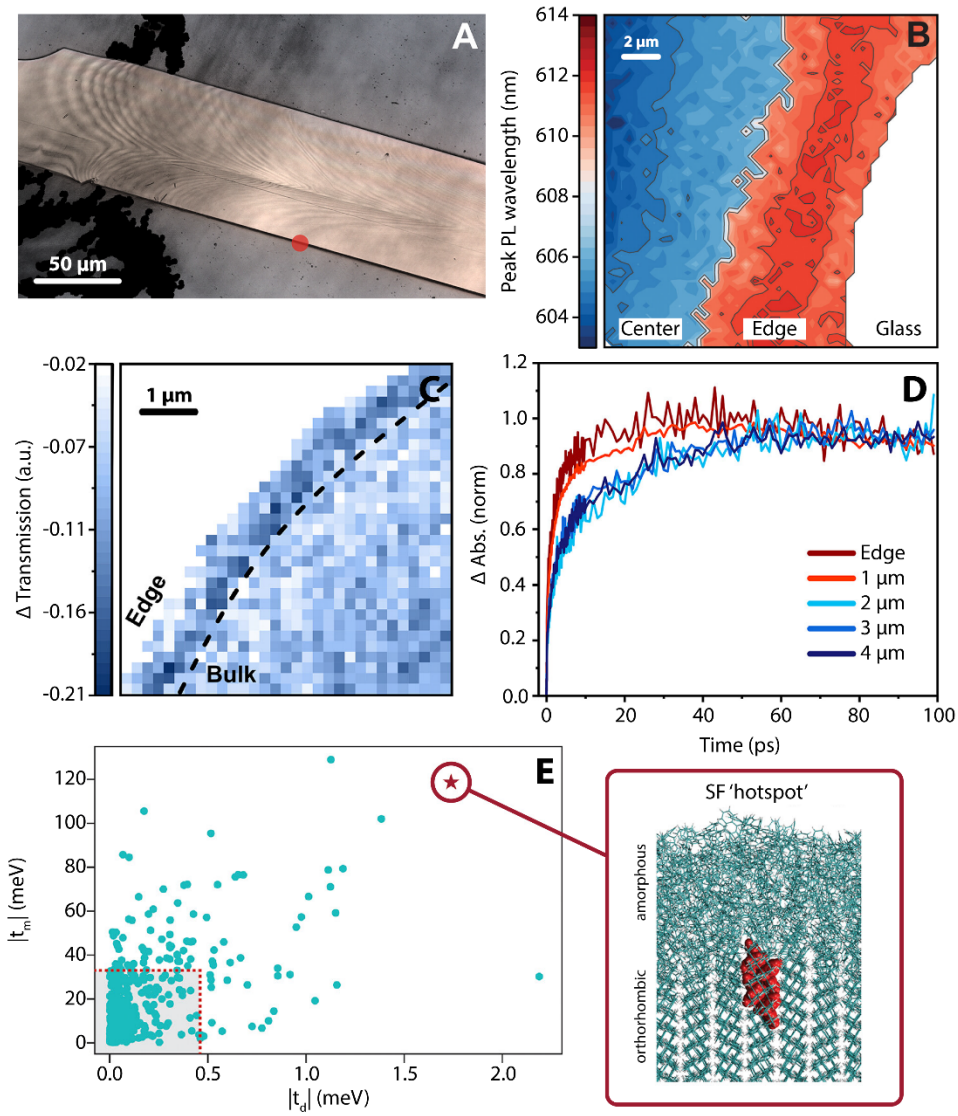

Figure 1: A) Optical image of a rubrene crystal. B) PL peak emission map of a rubrene crystal collected near the crystal edge. C) TAM image of a rubrene crystal visualizing the rise of the T_1 state of rubrene (510 nm) collected at 20 ps under 535 nm pump. D) Average transient absorption microscopy (TAM) kinetics of the T_1 photoinduced absorption rise (same as C) collected across different locations from the crystal edge for multiple crystals. E) SF electronic coupling (t_m and t_d) for a simulation of bulk orthorhombic rubrene capped with an amorphous layer at one time instance. Dashed red box denotes root mean square vales for t_m and t_d. Red box highlights one of the dimer pair SF 'hotspots'.

To further investigate the underlying properties of SF occurring in rubrene crystals, an example of which is shown in Fig 1A, Volek et al.[1] combined ultrafast optical spectroscopy with electronic structure calculations and molecular dynamics. Counterintuitively, their results suggest that SF rates increase in disordered regions at the edges of the crystal, as disorder removes the need of vibrational distortions to break symmetry and generate nonzero electronic couplings. Optical absorption microscopy is used to confirm the expected orthorhombic crystal structure based on the suppression of the 0-0 absorption band (533 nm). In addition, they find the absorption bands to be

broadened at the edge of the crystal in comparison to the center . This in combination with a red-shift of the emission at the crystal edge (Fig 1B) indicates increased structural disorder at the edges.

Femtosecond transient absorption microscopy (TAM) is used to elucidate how the structural disorder at the crystal edges of rubrene influence the rate and generation of triplet excitons. By monitoring the rubrene T_1 signal at 510 nm, a higher yield of triplets can be clearly observed as well as a higher rate of incoherent SF at the crystal edge (5.3 ps timescale) vs. the bulk of the crystal (20 ps) (Fig 1C,D). To explain this observation, simulations are used to determine the coupling strength which dictates the success of SF. Here, the authors focused on the two non-zero couplings t_m (mediated) and t_d (direct) between rubrene dimers. The results point to a thin disordered rubrene layer at the edge of the crystal, which disrupts the local symmetry of the orthorhombic rubrene. This symmetry breaking increases the electronic coupling, and thus, increases the rate of SF.

A key result of the work, however, is that the interface of the disordered and ordered rubrene acts as the hotspot of SF. In agreement with previous reports,[9] amorphous rubrene does not exhibit strong coupling, and thus, is not strongly SF active. On the other hand, the electronic coupling in the crystalline orthorhombic rubrene is nearly zero due to symmetry, resulting in poor SF.[1] However, at the interface between ordered and disordered rubrene (Fig 1E), the symmetry of the average rubrene dimer is broken, resulting in a nonzero coupling, and a fast rate of singlet fission. Here, the molecular dynamic results show many higher-coupling values of t_m and t_d than what would be typically calculated for orthorhombic rubrene, as shown by the dashed red box in Fig 1E.

In summary, the work by Roberts and coworkers previewed here demonstrates that disorder at the edge of rubrene crystals enhances the yield and rate of SF by increasing electronic coupling due to symmetry breaking. Overall, a closer look at the role of order vs. disorder, molecular level defects or imperfections on the local electronic coupling will be required to further advance applications of SF and TTA. This is particularly the case in materials such as rubrene, where both processes occur due to the triplet energy being roughly half of the singlet energy.

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Declaration of Interests

Lea Nienhaus is a member of the Editorial Advisory Board of Matter.

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